

## **ENCAPSULATED COMPOSITIONS**

## **BACKGROUND OF THE INVENTION**

#### **1. Technical Field Of The Invention.**

This invention broadly relates to a capsule comprised of a chemical composition surrounded by an exterior protective coating. The invention more particularly relates to the material employed to produce the exterior protective coating which surrounds the chemical composition contained in the capsule. The invention further relates to the release of the composition from the capsule.

## 2. Description Of The Prior Art And Problems Solved.

The prior art has long dealt with the problem of causing, or of creating the conditions to cause, a specified chemical composition to react in a specified environment or in a specified location at a specified time or over a specified period of time. This problem ordinarily stems from the need to initiate some chemical action in some desirable location prior to the start of, during or subsequent to the completion of some other action, and/or to cause the chemical action associated with a specified chemical composition to proceed over a desirable period of time. The related problems of controlling the time and controlling the place of reaction of a composition, as well as the solutions thereto, have been variously referred to in the art as delayed release, continuous release and controlled release and are referred to as such herein.

The prior art has addressed the problems referred to above and has developed various methods of controlling the introduction of an active chemical composition into reactive contact with an environment. The solutions to the problems have necessarily involved preventing reactive contact of the active chemical composition with an environment followed by enabling reactive contact to occur at some later time. One of the methods developed features the steps of preventing the mentioned reactive contact by completely covering a small quantity of the active chemical composition with a material to produce a capsule containing the composition

26 followed by introducing a number of such capsules into a designated environment wherein the  
27 composition is released from the capsule to enable reactive contact to thereby produce a  
28 desired chemical action.

29       The mode of release of the active chemical composition into reactive contact with the  
30 environment as contemplated by the prior art has proceeded along various different  
31 mechanisms. Such release mechanisms range from external crushing forces applied to the  
32 confining material, internal rupture and bursting forces applied to the confining material,  
33 disintegration of the confining material and diffusion or permeation of liquid through the  
34 confining material. Accordingly, the release mechanisms employed have featured the use of  
35 capsules which are crushed to rapidly release the enclosed chemical composition; capsules  
36 which rupture, or burst, to rapidly release the enclosed chemical composition; capsules which  
37 dissolve or disintegrate to rapidly release the enclosed composition; and capsules which do not  
38 rupture, but rely on diffusion or permeation, to gradually release the enclosed composition.

39       Chemical compositions known to have been involved in the controlled release thereof  
40 from a capsule have included medicines, pesticides, herbicides, cosmetics, laundry products,  
41 pigments, polymerization initiators, cross linking agents and viscosity reducing agents. A  
42 delayed and/or a continuous release of such compositions from enclosing capsules can offer  
43 the advantage of maximizing the effectiveness of the compositions or of minimizing or  
44 eliminating undesirable chemical or physical results or both.

45       The essential differences between the various controlled release methods of the prior  
46 art have resided in the nature of the material employed to form the exterior protective coating  
47 and the specific mechanism of the controlled release of the chemical composition from the  
48 confining material. Examples of such prior art methods are disclosed in various United States  
49 Patents including U.S. 4,756,844 (WALLES I), U.S. 4,741,401 (WALLES II), U.S. 4,923,753  
50 (WALLES III), U.S. 4,919,209 (KING) and U.S. 5,373,901 (NORMAN et al).

51       The prior art patents referred to above all disclose capsules containing active chemical  
52       compositions and the methods, that is, the mechanisms, of releasing the compositions from the  
53       capsules to enable the encapsulated chemicals to react with a composition in contact with the  
54       exterior of the capsules. Walles I illustrates its invention in terms of an encapsulated bleach as  
55       a laundry detergent additive. Walles II, King and Norman et al illustrate their inventions in terms  
56       of an encapsulated breaker for a fracturing fluid in a subterranean formation. Walles III  
57       illustrates its invention in terms of an encapsulated acid. The chemical compositions disclosed  
58       range from those which treat water based liquids to those which treat oil based liquids.  
59       Furthermore, the release mechanisms disclosed and/or referred to range from capsules which  
60       are crushed to rapidly release the enclosed agent; capsules which rupture, or burst, to rapidly  
61       release the enclosed agent; capsules which do not rupture, but rely on diffusion or permeation,  
62       to gradually release the enclosed agent; and capsules which dissolve or disintegrate to rapidly  
63       release the enclosed agent.

64       An important, if not the essential, feature of a method of controlling the release of a  
65       composition from a capsule is the timing of the release. This feature can be conveniently  
66       illustrated in connection with the release of a chemical from a capsule to reduce the viscosity of  
67       a fracturing fluid subsequent to the performance of a fracturing treatment of a subterranean  
68       formation. Reducing the viscosity of a fracturing fluid is referred to in the art as "breaking" and  
69       the viscosity reducing chemical is referred to as a "breaker." For purposes well known in the  
70       fracturing art, it is desirable that a fracturing fluid have a high viscosity during the performance  
71       of the fracturing process, but a low viscosity subsequent to the performance of the process. In  
72       this regard, a desired high viscosity is preferably to be observed in the vicinity of the  
73       subterranean formation to be treated and a desired low viscosity is also preferably to be  
74       observed in the vicinity of the subterranean formation, wherein the high viscosity condition

75 occurs prior to and during the performance of the fracturing treatment and the low viscosity  
76 condition occurs subsequent to the performance of the fracturing treatment.

77       Breakers, upon reactive contact with the fracturing fluid, can effectively produce the  
78 desired reduction of viscosity of the fluid, but the timing of the break, that is, when the break  
79 occurs, is of critical importance. Breakers, upon reactive contact with the fracturing fluid, begin  
80 to reduce the viscosity of the fluid. Accordingly, the problem to be solved is how to intimately  
81 mix the breaker with the fracturing fluid to enable essential reactive contact with the fluid, while  
82 at the same time delaying the time of reactive contact. This problem has been addressed and  
83 solved by placing the breaker in an enclosed volume called a capsule, the wall of which is a  
84 membrane which shields the fluid from the breaker to prevent reactive contact. The capsule  
85 containing the breaker is then intimately mixed with the high viscosity fluid, and the membrane,  
86 by one of the mentioned mechanisms, functions to release the breaker to enable reactive  
87 contact between the breaker and the fluid at some future time. The breaking of fracturing fluids  
88 and the use of encapsulated breakers to perform the task are subjects discussed in Norman et  
89 al, U.S. 5,373,901.

90       An important property of the material of construction of a capsule membrane is its ability  
91 to resist a caustic environment, either acid or base, exhibited by the chemical enclosed in, and  
92 thus in contact with, the interior of the capsule and by the chemical in contact with the exterior  
93 of the capsule. The sensitivity of the material of construction to a caustic environment is the  
94 subject of the disclosure of U.S. 4,923,753 (WALLES III) referred to above.

95       It is important from an operational point of view to be able to place chemical  
96 compositions of various natures, including caustic chemicals, in a capsule and to retain and  
97 maintain them therein shielded from the exterior environment until some desirable future time.  
98 A capsule thus constructed of a membrane material which will function to hold and maintain  
99 various diverse chemicals, such as, organic and inorganic caustics, salts and oxidizers, and

100 which will also function to release the chemicals at some desirable time is desired by the art.  
101 Accordingly, the material of construction of the capsule coating is the principal issue addressed  
102 in this invention.

103 **DISCLOSURE OF INVENTION**

104 **1. Summary Of The Invention.**

105 This invention is an article of manufacture and a method of using the article to treat a  
106 chemical composition in contact with the exterior of the article. The article of this invention is,  
107 thus, a capsule comprised of a hollow interior and an enclosing wall which is permeable to  
108 water or an aqueous solution. A first, water-soluble, chemical composition is enclosed, that is,  
109 encapsulated, in the hollow interior of the capsule by the wall of the capsule.

110 The permeable wall of the capsule, which is referred to herein as a membrane, is at  
111 least comprised of a first material and can be comprised of the first material together with a  
112 second material, in which case, the membrane is a composite material. When the membrane is  
113 a composite material the first material forms a supporting matrix, and the second material is  
114 fixed in the supporting matrix.

115 The first material is a urethane/vinyl hybrid polymer. It is not reactive with, soluble in or  
116 a solvent for the encapsulated first chemical composition, the second material, the liquid in  
117 contact with the exterior surface of the membrane or the chemical composition (referred to  
118 herein and in the appended claims as the second chemical composition) in contact with the  
119 exterior of the membrane.

120 The second material is a particulate solid and is different from the first material. The  
121 second material is not reactive with, soluble in or a solvent for the encapsulated first chemical  
122 composition, the first material, the liquid in contact with the exterior surface of the membrane or  
123 the second chemical composition.

124        The encapsulated first chemical composition can be substantially any water-soluble  
125        material which is not reactive with, soluble in or a solvent for the first material or the second  
126        material, but is reactive with and is, thus, useful to alter the chemical and/or physical properties  
127        of the second chemical composition in contact with the exterior surface of the membrane. The  
128        chemical nature of the encapsulated first chemical composition can include enzymes, and  
129        organic and inorganic acids, bases, salts and oxidizing agents. The encapsulated first chemical  
130        compositions are useful as medicines, pesticides, algaecides, herbicides, cosmetics, laundry  
131        products, pigments, polymerization initiators, cross linking agents and viscosity reducing  
132        agents. The encapsulated first chemical composition can be an additive for adjusting the  
133        setting properties of hydraulic cement and can be a breaker for a fracturing fluid, wherein the  
134        breaker can be a chemical selected from water-soluble enzymes, and organic or inorganic  
135        acids, bases, salts and oxidizing agents.

136        The second chemical composition, which as disclosed, is in contact with the exterior  
137        surface of the membrane can be substantially any water-soluble material which is not reactive  
138        with, soluble in or a solvent for the first material or the second material, but is reactive with the  
139        encapsulated first chemical composition.

140        2. Description Of The Preferred Embodiments.

141        The article of this invention is a capsule comprised of a solid, water-soluble first  
142        chemical composition preferably enclosed, that is, encapsulated, in a composite material. The  
143        composite material is comprised of a first material, which forms a matrix, in combination with a  
144        second material, different from the first material, which is fixed in the matrix. The phrase "fixed  
145        in the matrix," when employed in connection with the second material, means that the second  
146        material, while being firmly attached to the matrix, can be completely embedded within and,  
147        therefor, completely surrounded by, the matrix, or it can be partially embedded within and  
148        partially exposed at the interior surface or at the exterior surface of the matrix. It is understood

149 that the interior surface of the matrix is the interior surface of the membrane and the exterior  
150 surface of the matrix is the exterior surface of the membrane. As mentioned previously, the first  
151 material, which forms the supporting matrix of the membrane, is not reactive with, soluble in or  
152 a solvent for the encapsulated first chemical composition, the second material, the second  
153 chemical composition or a liquid in contact with the exterior surface of the membrane.

154 The first material is comprised of a urethane latex system and, more specifically, an  
155 aqueous polyurethane-vinyl polymer dispersion. The vinyl element preferred for use in this  
156 invention is acrylic in nature. Accordingly, the dispersion is more particularly referred to herein  
157 as a urethane/acrylic hybrid polymer. The aqueous polyurethane-vinyl polymer dispersion  
158 employed herein is disclosed in U.S. Patent 5,173,526 to Vijayendran et al. According to  
159 Vijayendran et al, the polyurethane-vinyl polymer dispersion is prepared by the simultaneous  
160 polymerization of a vinyl monomer and chain extension of an isocyanate-terminated  
161 polyurethane prepolymer in the presence of water. More particularly, Vijayendran et al disclose  
162 that, "the aqueous polymer is prepared by (a) forming a carboxy-containing, water dispersible,  
163 isocyanate-terminated polyurethane prepolymer, (b) adding a vinyl monomer mixture which  
164 contains a polyethylenically unsaturated monomer to the prepolymer to make a  
165 prepolymer/monomer mixture, (c) adding a tertiary amine to the prepolymer/monomer mixture,  
166 (d) dispersing the prepolymer/monomer mixture in water, (e) adding an oil soluble free radical  
167 initiator and a chain extender to the aqueous dispersion, and (f) polymerizing the vinyl  
168 monomers and completing the chain extension of the prepolymer by heating the aqueous  
169 dispersion." The process is said to provide an intimacy of interaction that cannot be achieved  
170 by blending. Accordingly, the first material, as defined above, is not a mere blend of a  
171 polyurethane and an acrylic polymer.

172 A urethane/acrylic hybrid polymer dispersion useful herein is commercially available in  
173 the form of an aqueous polymer dispersion from Air Products and Chemicals, Inc., under the  
174 Hybridur family of trademarks, two of which are Hybridur 540 and Hybridur 580.

175 The aqueous polyurethane-vinyl polymer dispersion employed herein is disclosed in  
176 Vijayendran et al to be useful as a protective coating for a solid substrate. It is disclosed that  
177 the dispersion is applied to the substrate by conventional flexographic or gravure methods and  
178 that the finished product protects the substrate from solvents, corrodants, and abrasives and  
179 that it exhibits good gloss and flexibility. The mentioned solid substrates include paper, metals,  
180 plastics and wood.

181 The first material can also be a reaction product. Accordingly, the urethane/acrylic  
182 hybrid polymer can be cross linked with a polyaziridine, carbodiimides, epoxies or metal ion  
183 cross linkers. An example of a polyaziridine polymer useful herein is pentaerythritol-tris-[ $\beta$ -  
184 (aziridinyl)propionate]. An example of a carbodiimide useful herein is 1,3-dicyclohexyl-  
185 carbodiimide. The urethane/acrylic hybrid polymer is preferably reacted with an aziridine cross  
186 linking agent to form the first material in the composite material employed in this invention.

187 The second material in the composite material is a particulate solid present in the  
188 composite material in an amount in the range of from greater than about 0 to about 50,  
189 preferably 10 to about 40 and still more preferably from about 20 to about 30 percent particulate  
190 solid by total weight of composite material. The particulate solid can have a size in the range of  
191 from about 1 to about 15 and preferably from about 2 to about 5 microns. As explained below  
192 in connection with the description of the capsule release mechanism, the particle size of the  
193 particulate solid in the composite material is preferably not less than 1 micron. In a  
194 manufacturing operation it is, of course, difficult to completely exclude all particulate solids  
195 having a size of less than 1 micron, however, it is preferred that concentration of particulate

196      solids having a size less than 1 micron should not exceed about 25 percent by weight of  
197      particulate solids present in the composite material.

198            The second material can include silica, calcium carbonate, titanium dioxide, barium  
199            sulfate, calcium sulfate, similar such materials and mixtures thereof.

200            The first chemical composition encapsulated within the composite material of this  
201          invention can be substantially any water-soluble material, limited as previously stated, selected  
202          from the group consisting of enzymes, and organic and inorganic acids, bases, salts and  
203          oxidizing agents. More specifically, the chemical compositions preferably include alkali, alkaline  
204          earth metal and ammonium halides, oxides, hydroxides, carbonates, bicarbonates, perborates,  
205          peroxides, percarbonates, bisulfates, bromates and sulfates. The chemical agents can also  
206          include liquids which have been adsorbed on solid substrates, such as, diatomaceous earth and  
207          then encapsulated.

208            Specific examples of chemical agents useful herein as the first chemical composition  
209          include hemicellulase, sodium bisulfate, calcium chloride, lithium hydroxide, potassium  
210          carbonate, salts of phosphonic acid, sodium persulfate, ammonium persulfate, magnesium  
211          oxide, citric acid, fumaric acid, sodium citrate, sodium fumarate, polyglycolic acid, sulfamic acid,  
212          potassium bromate, sodium bromate and tetraethylpentamine.

213            In one embodiment, the first chemical composition can be a breaker for an aqueous  
214          fracturing fluid, examples of which include the oxidizing agents, sodium persulfate and  
215          potassium persulfate. In another embodiment, the first chemical composition can be an  
216          aqueous viscosifying agent such as guar gum, hydroxy propyl guar, hydroxy ethyl cellulose and  
217          xanthan gum. In still another preferred embodiment, the first chemical composition can be an  
218          additive for adjusting the setting properties of hydraulic cement such as accelerators, retarders  
219          and viscosifiers, examples of which include calcium chloride, calcium lignosulfonate and

220 hydroxy ethyl cellulose. In yet another embodiment, the first chemical composition can be a pH  
221 adjusting material such as lithium hydroxide and potassium carbonate.

222 The capsule of this invention can be made by utilizing a fluidized bed process, one  
223 version of which is referred to as the Wurster process and a modification thereof which employs  
224 a top spray method. Equipment employed to produce the capsule is available from Glatt Air  
225 Techniques, Inc. Ramsey, New Jersey. A specific apparatus available from Glatt Air  
226 Techniques is the WSG 5 fluidized bed coater, the use of which is illustrated in the examples  
227 set out below.

228 In a preferred method of manufacture, the capsule of this invention is made by first  
229 admixing the second material, the particulate solid, with the first material, the urethane/acrylic  
230 hybrid polymer, in the proportions above disclosed. The cross linker can then be admixed with  
231 the hybrid polymer and solid in an amount in the range of from about 0 to about 5, and  
232 preferably from about 1 to about 3, per cent cross linker by weight of hybrid polymer.  
233 Thereafter, utilizing the fluidized bed process, the first chemical composition to be encapsulated  
234 is introduced into a spray chamber and suspended therein by a flow of gas, such as air, while  
235 the mixture of hybrid polymer, solid and cross linker are sprayed against the suspended  
236 chemical composition to thereby form the capsule. The combination of chemical composition to  
237 be encapsulated and composite material is adjusted to produce a capsule having in the range  
238 of from about 10 to about 50, and preferably from about 20 to about 40 percent composite  
239 material by weight of capsule.

240 As previously indicated, the capsules of this invention can be made by well known  
241 fluidized bed encapsulation techniques wherein solid particles of the first chemical composition  
242 are sprayed with the composite material while the particles are suspended in a flow of air or  
243 other gas within a spray chamber. There is no known limitation on the particle size of the  
244 chemical composition being encapsulated, but a particle size in the range of from about 10 to

245 about 60 mesh US Sieve series is conveniently employed. Thus, with respect to the above  
246 range, particles of a size which do not pass a 10 mesh screen and particles which do pass a 60  
247 mesh screen are preferably not employed. To maintain product uniformity with respect to  
248 performance, the first chemical composition, prior to encapsulation, is preferably sized to  
249 remove a substantial portion of any fines or agglomerations of chemical particles. In this  
250 manner, the thickness of the membrane wall of the capsules will have, within a relatively narrow  
251 range, a substantially uniform thickness and the capsules will exhibit generally uniform release  
252 control properties.

253         Generally, the capsule of this invention is prepared having a membrane coating  
254 consisting of the cross linked urethane/acrylic hybrid polymer and particulate mixture, i.e. the  
255 composite material, of a certain thickness and permeability to obtain the desired controlled  
256 release of the first chemical composition for a particular dissolved second chemical composition  
257 to be treated. The quantity and size of the particulate present in the composite material will  
258 significantly effect the permeability of the created membrane coating.

259         The particle size of the capsule varies depending upon the desired amount of chemical  
260 composition to be released and the desired rate at which the composition is to be released. For  
261 example, the thicker the membrane, generally the slower the release since it takes longer for an  
262 aqueous liquid in contact with the exterior surface of the capsule to diffuse, i.e., permeate,  
263 through the wall of the membrane to dissolve the agent and then diffuse, i.e., permeate, back  
264 through the membrane. This relationship, however, can be modified by changing the particle  
265 size of the second material present in the matrix. If the second chemical composition to be  
266 treated by the first chemical composition is a fracturing fluid containing a proppant, then it is  
267 preferred that the particle size of the capsule be substantially equal to or smaller than the  
268 particle size the proppant.

269        In the method of operation, an aqueous liquid in contact with the exterior surface of the  
270        capsule gradually passes, by diffusion, through the membrane into the hollow interior of the  
271        capsule and therein contacts and dissolves the first chemical composition encapsulated therein  
272        to form a solution of the composition in water. It is to be understood that the aqueous solution  
273        in contact with the exterior surface of the capsule can be present in the contact location as a  
274        natural constituent of the environment or introduced into the environment prior to, together with  
275        or subsequent to the introduction of the capsule.

276        The solution formed within the capsule then gradually passes, by diffusion, from the  
277        hollow interior of the capsule through the membrane to the exterior of the capsule to there  
278        contact and react with the second chemical composition.

279        The described operating mechanism, which consists in diffusion of an aqueous liquid in  
280        contact with the exterior of the capsule into the capsule and diffusion of a formed solution out of  
281        the capsule, requires an extended period of time to be completed to thereby avoid release of all  
282        of the first chemical composition over a very short span of time.

283        It is believed that the operating mechanism of this invention is driven by very small  
284        pressure differences between the interior and exterior of a capsule. Thus, when the pressure in  
285        the interior of the capsule is less than the pressure on the exterior of the capsule, the aqueous  
286        liquid passes through the membrane to the interior of the capsule to contact and dissolve the  
287        first chemical composition. Upon dissolution, pressure within the interior of the capsule  
288        increases to a value greater than the pressure on the exterior of the capsule. Accordingly,  
289        upon this pressure increase, the formed solution passes through the membrane to the exterior  
290        of the capsule. In some instances, depending upon the nature of the aqueous liquid and/or the  
291        nature of the agent, a gas may be produced within the interior of the capsule. In spite of the  
292        described pressure actuated mechanism, it is believed that the pressure stresses do not cause

293 the capsule to rupture, break, dissolve or disintegrate. The capsule remains intact during the  
294 entire diffusion process.

295       The particle size of the second material, which is fixed in the matrix, plays an important  
296 role in the diffusion process. In this regard, it is believed that capsules which contain particles  
297 having a size of less than about 1 micron, i.e., submicron particles, do not operate to dissipate  
298 internal pressure, generated as described above, at a rate sufficiently great to prevent rupture  
299 of the capsule. Capsules which contain particles having a size of 2 microns and greater,  
300 preferably about 5 microns, fixed in the matrix, do operate to dissipate internal pressure at a  
301 rate sufficient to prevent rupture of the capsule.

302       The capsule of this invention functions to slowly release all of the encapsulated first  
303 chemical composition over an extended period of time as contrasted with a rapid release of all  
304 of the encapsulated agent over a very short period of time. The capsule operates as stated,  
305 without change in the desired rate of release of the encapsulated composition, in the presence  
306 of liquids at temperatures in the range of from about 50 to about 325<sup>0</sup> F and at pH values in the  
307 range of from about 2 to about 11.

308       The above disclosure has concentrated on the permeable wall of the capsule of this  
309 invention as consisting solely of a defined first material or as a composite material consisting of  
310 a combination of the first material and a defined particulate second material. However, in  
311 another aspect, the membrane of this invention, as defined above, can serve as an undercoat  
312 or a primer coat for a third material, such as an acrylic, which would not be compatible with the  
313 encapsulated first chemical composition if placed in direct contact therewith. It has been  
314 discovered that the membrane of this invention can successfully function as a barrier between  
315 an encapsulated chemical and a coating which, for some reason, would not ordinarily be  
316 compatible with the encapsulated chemical.

## **EXAMPLES**

The following examples are provided to illustrate the manufacture and use of the invention and to contrast its operation with the prior art.

### Example A

## **Method for Preparing Membrane Material**

This invention is a capsule having a permeable wall, referred to as a membrane, and a hollow interior containing a water soluble chemical composition. The membrane is comprised of a first material, previously described as a supporting matrix, which can have fixed therein a second material, previously referred to as a particulate. This example discloses a method of preparing the said first material.

Accordingly, 31.6 pounds of an aqueous polymer dispersion containing 40 percent by weight solids and 60 percent by weight water was introduced into a five gallon container. The solids component of the aqueous polymer dispersion contained 50 percent by weight polyurethane and 50 percent by weight vinyl polymer. Thereafter, 61.0 grams of a silicone surface additive and 74.4 grams of a silicone defoamer were introduced into the container containing the polymer dispersion to form a mixture which was blended with moderate agitation for 15 minutes to form a homogeneous mixture. Then 1004.6 grams of coalescent solvent was added to the homogenous mixture to form the completed mixture and agitation was continued for an additional two hours. The completed mixture, referred to herein as Hybrid Urethane A, contained about 37 percent by weight solids and had a density of about 8.5 pounds per gallon.

The aqueous polymer dispersion used was a product available from Air Products and Chemicals, Inc., under the trademark Hybradur 540, said to be prepared by the process disclosed in U.S. Patent 5,173,526. The silicone defoamer used was identified as BYK-024 available from BYK-Chemie. The silicone surface additive used was identified as BYK-333

available from BYK-Chemie. The coalescent solvent used was identified as glycol ether DPM available from Chem Central.

### Example B

## Method for Preparing Membrane Material

The procedure described in Example A, above, for preparing Hybrid Urethane A did not include the step of adding a particulate which has been called the second material of the composite material of this invention. This example modifies the procedure of Example A and describes the preparation of four materials, Hybrid Urethane B, Hybrid Urethane C, Hybrid Urethane D and Hybrid Urethane E, each of which includes the first material and the second material of the composite material of this invention.

Accordingly, a blend consisting of quantities of the aqueous polymer dispersion of Example A, the defoamer of Example A and the surface additive of Example A and at least one particulate were combined to form a precursor. Thereafter, a further quantity of the aqueous polymer dispersion of Example A and a quantity of the coalescent solvent of Example A were added to the precursor to complete the preparation of the composite material.

Aqueous polymer dispersion, defoamer and surface additive were introduced into a container of suitable size and moderately agitated to combine the ingredients. Thereafter, the particulate was added with moderate to high agitation for at least about one hour to thoroughly mix all of the combined ingredients to thereby form the precursor. Then, a further quantity of aqueous polymer dispersion was added to the precursor with moderate agitation followed by addition of the coalescent solvent. Agitation was continued for a period of at least about 30 minutes to complete the preparation of the composite material.

The particulates employed were silica, available from US Silica under the identifier MIN-U-SIL 5, and calcium carbonate, available from OMYA, Inc., under the identifier OMYABARB 3T and 4T.

366           The recipes and physical properties of Hybrid Urethanes B, C, D and E are provided in  
367           Tables 1 and 2, respectively, below.

368           TABLE 1

369           Recipes for Hybrid Urethanes Containing Particulates

RECIPE FOR COMPOSITE MATERIAL							
Hybrid Urethane	Precursor Content					Precursor Additives	
	basic contents			particulates		basic contents	
	aqueous polymer dispersion grams	defoamer grams	surface additive grams	silica grams	calcium carbonate grams	aqueous polymer dispersion grams	coalescent solvent grams
B	5287.8	28.60	35.50	886.3	-	1362.0	467.2
C	5035.6	29.10	35.40	-	879.30	1789.1	468.7
D	5314.8	34.70	42.30	867.3	218.40	2816.5	869.7
E	4041.9	61.19	74.25	1682.9	189.84	9982.7	988.1

377           TABLE 2

378           Physical Properties of Hybrid Urethanes of Table 1

PHYSICAL DATA			
Hybrid Urethane	Density lb/gal	Solids Concentration % by weight	Viscosity centipoise
B	9.306	44.7	176.2
C	9.148	44.8	121.2
D	9.172	44.7	95.2
E	9.394	44.7	175.6

385           Note: The viscosity of the polymer was measured using a Brookfield RVDV 1 viscometer with a  
386           #1 spindle rotating at 50 rpm

### **Example C**

## **Standard Procedure for Preparing Encapsulated Chemical Compositions**

In the examples which follow a standard procedure was employed to encapsulate a  
cal composition in a membrane. A description of the standard procedure is set out in this  
example.

Capsules were produced using a WSG 5 fluidized bed coater available from Glatt Air Techniques. The coating was applied using a top spray insert. The spray head used was a Schlick Model 970 spray nozzle available from Orthos Liquid Systems Inc. with a 1.2-mm insert. Depending on the product, either a 80 mesh screen or a 10 micron sock was installed between the expansion chamber and the filter chamber to act as the filter. The air used to fluidize the product was heated in order to maintain a bed temperature in the range of from about 88 to about 106<sup>0</sup> F. The air used to atomize the coating at the spray head was pressurized to 37 psi. After all of the coating was applied, the bed temperature was allowed to increase to a value in the range of from about 105 to about 110<sup>0</sup> F for about five minutes to cure the coating.

## **EXAMPLE 1**

## Encapsulation of Lithium Hydroxide

The coating material disclosed in Norman et al (U.S. 5,373,901) was used in an attempt to encapsulate lithium hydroxide. Thus, 628.2 grams of water and 55.8 g of polyaziridine crosslinker were added to 3316.0 grams of the coating material disclosed in Norman et al. The fluidized bed coater of Example C was charged with 7000 grams of anhydrous lithium hydroxide. The lithium hydroxide employed did not include particles which were small enough to pass through a 60 mesh screen. The lithium hydroxide was not successfully encapsulated. Varying the processing conditions did not produce capsules containing lithium hydroxide. It was apparent that lithium hydroxide produced a negative effect on the application of the coating material disclosed by Norman et al.

412

## EXAMPLE 2

413

### Encapsulation of Lithium Hydroxide

414       The polyaziridine crosslinker of Example 1 (36.5 grams) and 62.2 grams of water were  
415       added to 3651.4 grams of the Hybrid Urethane A of Example A. The resulting mixture was  
416       stirred for 10 minutes. The fluidized bed coater of Example C was charged with 5000 grams of  
417       anhydrous lithium hydroxide. The lithium hydroxide employed consisted of particles which were  
418       small enough to pass through a 10 mesh screen but did not include particles which were small  
419       enough to pass through a 50 mesh screen. The bed temperature was maintained at a value in  
420       the range of from about 94 to about 100<sup>0</sup> F. The coating mixture was initially applied at a rate  
421       of about 40 g/min, and then increased to a rate of about 52 g/min. A total of 3378.5 grams of  
422       coating mixture was successfully added. After the completion of the coating operation it was  
423       observed that the lithium hydroxide had experienced an apparent weight increase of  
424       approximately 20%, which increase was attributed to the Hybrid Urethane A coating placed  
425       thereon.

426

## EXAMPLE 3

427

### Encapsulation of Lithium Hydroxide

428       The coating material described in Norman et al (U.S. 5,373,901) was used in an attempt  
429       to over coat the capsules produced in Example 2. Thus, 413.0 grams of water and 57.4 grams  
430       of the polyaziridine crosslinker of Example 1 were added to 2029.8 grams of the coating  
431       material described in Norman et al. The fluidized bed coater of Example C was charged with  
432       4000 grams of the capsules produced in Example 2. The bed temperature was maintained at a  
433       value in the range of from about 100 to about 106<sup>0</sup> F. A total of 2227.2 grams of the coating  
434       material of Norman et al was successfully applied resulting in a weight gain of the capsules of  
435       approximately 20%.

Example 3, above, illustrates the effectiveness of the Hybrid Urethane A of Example 2 as a primer coat. As shown in Example 1, lithium hydroxide could not be directly coated with the material disclosed in Norman et al, accordingly, a delayed release capsule containing lithium hydroxide directly encapsulated by the material disclosed by Norman et al could not be produced. However, by first coating lithium hydroxide with the Hybrid Urethane A, the resulting capsules could then be coated with the material disclosed by Norman et al. The Hybrid Urethane A thus shielded the material of Norman et al from the lithium hydroxide.

**EXAMPLE 4**

The capsules produced in Examples 2 and 3 were contacted with a soak solution consisting of dilute sodium hydroxide at room temperature to cause the release of the encapsulated lithium hydroxide. The soak solution was prepared by dissolving 3.60 grams of sodium hydroxide, 12.0 ml bromocresol green indicator solution and 0.9 ml of nonylphenol surfactant in 900 ml of deionized water. A quantity of encapsulated lithium hydroxide from Example 2 was weighed into a first 125-ml Erlenmeyer flask and an equal quantity of encapsulated lithium hydroxide from Example 3 was weighed into a second 125-ml Erlenmeyer flask. A 5.0 ml quantity of the soak solution was added to each flask. After 10 minutes of exposure a sample of soak solution from each flask was titrated to the end point with 0.5173 M HCl and an additional 5.0 ml soak solution was added. The titration procedure was repeated at intervals of 30 and 60 minutes. The results of the titrations are provided in Table 3.

455  
Table 3

Time minutes	Lithium Hydroxide Released, %	
	Example 2	Example 3
10	14.9	9.69
30	40.0	33.40
60	72.9	60.00

456 Example 4 demonstrates that the Hybrid Urethane A coating material functions as a  
457 primer coat (Example 3) and also as a primary barrier coating (Example 2). It, accordingly,  
458 operates in a dual capacity. Since the particles produced in Example 2 included less coating  
459 than those produced in Example 3, the rate of release of lithium hydroxide in Example 2 was  
460 greater than the rate in Example 3.

461  
**EXAMPLE 5**

462  
**Encapsulation of Potassium Carbonate**

463 The coating material disclosed in Norman et al was used in an attempt to encapsulate  
464 potassium carbonate. Thus, 1011.5 grams of water were added to 5988.5 grams of the coating  
465 material disclosed in Norman et al. The fluidized bed coater of Example C was charged with  
466 9000 grams of potassium carbonate. The potassium carbonate employed did not include  
467 particles which were small enough to pass through a 40 mesh screen. The potassium  
468 carbonate was not successfully encapsulated. Varying the processing conditions did not  
469 produce capsules containing potassium carbonate. It was apparent that potassium carbonate  
470 produced a negative effect on the application of the coating material disclosed by Norman et al.  
471  
472  
473  
474  
475

476

## EXAMPLE 6

477

### Encapsulation of Potassium Carbonate

478

The polyaziridine crosslinker of Example 1 (31.2 grams) and 53.0 grams of water were

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added to 3124.0 grams of the Hybrid Urethane A of Example A. The resulting mixture was

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stirred for 10 minutes. The fluidized bed coater of Example C was charged with 7000 grams of

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potassium carbonate. The potassium carbonate employed consisted of particles which were

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small enough to pass through a 10 mesh screen but did not include particles which were small

483

enough to pass through a 60 mesh screen. The bed temperature was maintained at a value in

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the range of from about 100 to about 105<sup>0</sup> F. The coating mixture was applied at a rate of

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about 40 g/min. A total of 3082.0 grams of coating mixture was successfully added. After the

486

completion of the coating operation it was observed that the potassium carbonate had

487

experienced an apparent weight increase of approximately 16%, which increase was attributed

488

to the Hybrid Urethane A coating placed thereon.

489

## EXAMPLE 7

490

### Encapsulation of Potassium Carbonate

491

The coating material described in Norman et al (U.S. 5,373,901) was used in an attempt

492

to over coat the capsules produced in Example 6. Thus, 1036.6 grams of water and 92.1

493

grams of the polyaziridine crosslinker of Example 1 were added to 5471.3 grams of the coating

494

material described in Norman et al. The fluidized bed coater of Example C was charged with

495

6500 grams of the capsules produced in Example 6. The bed temperature was maintained at a

496

value in the range of from about 100 to about 106<sup>0</sup> F. A total of 6,190.5 grams of the coating

497

material of Norman et al was successfully applied resulting in a weight gain of the capsules of

498

approximately 30%.

499

Example 7, above, illustrates the effectiveness of the Hybrid Urethane A of Example 6

500

as a primer coat. As shown in Example 5, potassium carbonate could not be directly coated

501 with the material disclosed in Norman et al. Accordingly, a delayed release capsule containing  
502 potassium carbonate directly encapsulated by the material disclosed by Norman et al could not  
503 be produced. However, by first coating potassium carbonate with the Hybrid Urethane A, the  
504 resulting capsules could then be coated with the material disclosed by Norman et al. The  
505 Hybrid Urethane A thus shielded the material of Norman et al from the potassium carbonate.

506 **EXAMPLE 8**

507 The capsules produced in Examples 6 and 7 were contacted with a soak solution at  
508 temperatures of 75 and 150° F to cause the release of the encapsulated potassium carbonate.  
509 The soak solution was prepared by dissolving 4 drops of bromocresol green indicator solution  
510 and 0.1% of nonylphenol surfactant in 10 ml of deionized water. A quantity of encapsulated  
511 potassium carbonate from Example 6 was weighed into a first 50-ml Erlenmeyer flask and an  
512 equal quantity of encapsulated potassium carbonate from Example 7 was weighed into a  
513 second 50-ml Erlenmeyer flask. At the indicated times, the samples were titrated to the end  
514 point with 0.5055 M HCl. The results of the titrations are provided in Table 4.

515 **TABLE 4**

Time minutes	Potassium Carbonate Released, %			
	75° F		150° F	
	Example 6	Example 7	Example 6	Example 7
20	23.0	0.99	51.2	6.22
40	43.0	2.04	77.7	19.50
60	60.3	3.70	88.4	36.70
90	73.1	5.58	94.0	63.80
120	80.5	7.57	95.3	82.70
180	88.2	11.5	96.0	95.30
240	91.7	14.4	-	-

Example 8 demonstrates that the Hybrid Urethane A coating material functions as a primer coat (Example 7) and also as a primary barrier coating (Example 6). It, accordingly, operates in a dual capacity. Since the particles produced in Example 6 included less coating than those produced in Example 7, the rate of release of potassium carbonate in Example 6 was greater than the rate in Example 7. Example 8 further demonstrates that increase in temperature of contact increases the rate of release of encapsulated material

### **EXAMPLE 9**

## Encapsulation of Magnesium Oxide

The polyaziridine crosslinker of Example 1 (40.8 grams) and 69.5 grams of water were added to 4089.6 grams of the Hybrid Urethane A of Example A. The resulting mixture was stirred for 10 minutes. The fluidized bed coater of Example C was charged with 7000 grams of prilled magnesium oxide. The bed temperature was maintained at a value in the range of from about 88 to about 95<sup>0</sup> F. The coating mixture was applied at a rate of about 60 g/min.

In one run a total of 1217.5 grams of coating mixture was successfully added. In a second run a total of 4187.1 grams of coating mixture was successfully added. After the completion of the coating operation it was observed that the magnesium oxide had experienced an apparent weight increase of approximately 6% in the first run and approximately 18% in the second run. The weight increase was attributed to the Hybrid Urethane A coating placed thereon.

## **EXAMPLE 10**

To determine the effectiveness of the coated materials prepared in Example 9, samples were tested by observing the pH change of aqueous solutions containing active magnesium oxide. In this regard, 2.13 grams of the 6% material and 2.44 grams of the 18% material as prepared in Example 9 were employed, each of which contained 2.00 grams of active magnesium oxide. These two samples were compared with 2.00 grams of un-coated

550 magnesium oxide. Accordingly, 100 ml of deionized water containing 1% nonylphenol  
551 surfactant was placed into each of three 250 ml beakers equipped with a stirring bar. The  
552 beakers were placed in turn on a stirring plate and a temperature compensated pH probe was  
553 immersed into the solution in each beaker. After the pH stabilized, a 2.00 gram active MgO  
554 sample was added to each beaker. The pH of the solution in each beaker was recorded versus  
555 time. The results of the pH measurements are provided in Table 5.

556 TABLE 5

Time minutes	pH of Solution		
	Coating %		
	0	6	18
0.0	5.00	6.02	4.85
0.5	8.90	6.20	4.81
1.0	9.28	6.41	4.83
2.0	9.87	6.92	4.92
3.0	10.33	7.67	4.96
4.0	10.54	8.16	5.02
5.0	10.66	8.36	4.87
7.0	10.78	8.80	5.04
10.0	10.89	9.00	5.06
15.0	11.00	9.32	5.50
30.0	11.16	9.79	5.47
60.0	11.23	10.12	5.97
90.0		10.29	6.25
120.0		10.31	6.36
180.0			6.95

574 The results obtained in Example 10, above, demonstrate the Hybrid Urethane A  
575 operates as a barrier coating for magnesium oxide.

576

### Example 11

577

#### Encapsulation of Ammonium Persulfate

578

The polyaziridine crosslinker of Example 1 (42.3 grams) and 96.0 grams of water were

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added to 4262.0 grams of the Hybrid Urethane A of Example A. The resulting mixture was

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stirred for 10 minutes. The fluidized bed coater of Example C was charged with 7000 grams of

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ammonium persulfate. The ammonium persulfate employed consisted of particles which were

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small enough to pass through a 20 mesh screen but did not include particles which were small

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enough to pass through a 50 mesh screen. The bed temperature was maintained at a value in

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the range of from about 100 to about 105<sup>0</sup> F. The coating mixture was applied at a rate of in

585

the range of from about 40 to about 60 g/min. A total of 4170.6 grams of coating mixture was

586

successfully added. After the completion of the coating operation it was observed that the

587

ammonium persulfate had experienced an apparent weight increase of approximately 18%,

588

which increase was attributed to the Hybrid Urethane A coating placed thereon.

589

The coated particles produced as described above were further treated to increase the

590

weight increase to a total of 36 %. Accordingly, to 4649.4 grams of Hybrid Urethane A was

591

added 46.3 grams of polyaziridine crosslinker and 95.0 grams of water. The resulting mixture

592

was stirred for 10 minutes. The fluidized bed coater was charged with 6000 grams of the

593

particles as prepared above. The bed temperature was maintained at a value in the range of

594

from about 99 to about 105<sup>0</sup> F. The coating material was applied at a rate in the range of from

595

about 60 to about 70 g/min. A total of 4559.9 grams of coating material was added resulting in

596

a weight gain of approximately 36%.

597

### EXAMPLE 12

598

#### Encapsulation of Ammonium Persulfate

599

The polyaziridine crosslinker of Example 1 (33.2 grams) and 96.4 grams of water were

600

added to 3571.1 grams of the Hybrid Urethane E of Example B. The resulting mixture was

601 stirred for 10 minutes. The fluidized bed coater of Example C was charged with 5000 grams of  
602 ammonium persulfate. The ammonium persulfate employed consisted of particles which were  
603 small enough to pass through a 20 mesh screen but did not include particles which were small  
604 enough to pass through a 40 mesh screen. The bed temperature was maintained at a value in  
605 the range of from about 93 to about 98<sup>0</sup> F. The coating mixture was applied at a rate of in the  
606 range of from about 60 to about 76 g/min. A total of 2842.3 grams of coating mixture was  
607 successfully added. After the completion of the coating operation it was observed that the  
608 ammonium persulfate had experienced an apparent weight increase of approximately 20%,  
609 which increase was attributed to the Hybrid Urethane E coating material placed thereon.

610 The coated particles produced as described above were further treated to increase the  
611 weight increase to a total of 28%. Accordingly, to 1351.6 grams of Hybrid Urethane E were  
612 added 12.3 grams of polyaziridine crosslinker and 36.1 grams of water. The resulting mixture  
613 was stirred for 10 minutes. The fluidized bed coater was charged with 5200 grams of the  
614 particles as prepared above. The bed temperature was maintained at a value in the range of  
615 from about 93 to about 98<sup>0</sup> F. The coating material was applied at a rate of from about 76  
616 g/min. A total of 1313.6 grams of coating material was added resulting in a weight gain of  
617 approximately 28%.

618 The coated particles produced as described above were further treated to increase the  
619 weight increase to a total of 36%. Accordingly, to 1448.2 grams of Hybrid Urethane E was  
620 added 13.2 grams of polyaziridine crosslinker and 38.6 grams of water. The resulting mixture  
621 was stirred for 10 minutes. The fluidized bed coater was charged with 5000 grams of the  
622 particles as prepared above. The bed temperature was maintained at a value in the range of  
623 from about 93 to about 98<sup>0</sup> F. The coating material was applied at a rate of from about 76  
624 g/min. A total of 1421.8 grams of coating material was added resulting in a weight gain of  
625 approximately 36%.

626

### EXAMPLE 13

627       Release tests were performed with the capsules produced in Example 11 and Example  
628       12, above, and the results were compared with results obtained with capsules of coated  
629       ammonium persulfate obtained following the procedure disclosed in Norman et al. The test  
630       procedure disclosed in Example II of the Norman et al was employed in the performance of the  
631       tests in this example. The test results are recorded in Table 6.

632

TABLE 6

Time hours	Ammonium Persulfate Released, %		
	Example 11	Example 12	U.S. 5,373,901
0.5	0.41	-	0.88
1.0	1.69	7.47	2.08
2.0	6.42	16.20	13.00
3.0	15.40	-	53.70
3.5	-	46.80	-
4.0	28.20	-	70.80
4.5	-	59.50	-
5.0	37.70	-	74.30
6.0	46.00	-	76.20
7.0	52.30	-	-

645       The above data clearly illustrates the usefulness of Hybrid Urethane E as a barrier  
646       coating for ammonium persulfate and the improved release profiles as compared to that  
647       obtained by employing the coating material of U.S. 5,373,901 to Norman et al.

648

## EXAMPLE 14

649

### Encapsulation of Sulfamic Acid

650       The polyaziridine crosslinker of Example 1 (37.7 grams) and 49.9 grams of water were  
651       added to 4113.3 grams of the Hybrid Urethane A of Example A. The resulting mixture was  
652       stirred for 10 minutes. The fluidized bed coater of Example C was charged with 5500 grams of  
653       sulfamic acid. The sulfamic acid employed consisted of particles which were small enough to  
654       pass through a 10 mesh screen but did not include particles which were small enough to pass  
655       through a 50 mesh screen. The bed temperature was maintained at a value in the range of  
656       from about 93 to about 98<sup>0</sup> F. The coating mixture was applied at a rate of from about  
657       about 40 to about 55 g/min. A total of 3716.2 grams of coating mixture was successfully added.  
658       After the completion of the coating operation it was observed that the sulfamic acid had  
659       experienced an apparent weight increase of approximately 20%, which increase was attributed  
660       to the Hybrid Urethane A coating material placed thereon.

661       The coated particles produced as described above were further treated to increase the  
662       weight increase to a total of 28%. Accordingly, to 1351.6 grams of Hybrid Urethane A were  
663       added 12.3 grams of polyaziridine crosslinker and 36.1 grams of water. The resulting mixture  
664       was stirred for 10 minutes. The fluidized bed coater was charged with 5000 grams of the  
665       particles as prepared above. The bed temperature was maintained at a value in the range of  
666       from about 93 to about 98<sup>0</sup> F. The coating material was applied at a rate of from about 60  
667       g/min. A total of 1356.0 grams of coating material was added resulting in a weight gain of  
668       approximately 28%.

669       The coated particles produced as described above were further treated to increase the  
670       weight increase to a total of 36%. Accordingly, to 1448.2 grams of Hybrid Urethane A was  
671       added 13.2 grams of polyaziridine crosslinker and 38.6 grams of water. The resulting mixture  
672       was stirred for 10 minutes. The fluidized bed coater was charged with 4300 grams of the

particles as prepared above. The bed temperature was maintained at a value in the range of from about 93 to about 98° F. The coating material was applied at a rate of from about 60 g/min. A total of 1414.5 grams of coating material was added resulting in a weight gain of approximately 36%.

### Example 15

## Encapsulation of Sulfamic Acid

The polyaziridine crosslinker of Example 1 (14.1 grams) and 41.2 grams of water were added to 1544.7 grams of the Hybrid Urethane B of Example B. The resulting mixture was stirred for 10 minutes. The fluidized bed coater of Example C was charged with 5000 grams of sulfamic acid. The sulfamic acid employed consisted of particles which were small enough to pass through a 10 mesh screen but did not include particles which were small enough to pass through a 50 mesh screen. The bed temperature was maintained at a value in the range of from about 93 to about 98<sup>0</sup> F. The coating mixture was applied at a rate of in the range of from about 50 to about 70 g/min. A total of 1516.2 grams of coating mixture was successfully added. After the completion of the coating operation it was observed that the sulfamic acid had experienced an apparent weight increase of approximately 12%, which increase was attributed to the Hybrid Urethane A coating material placed thereon.

The coated particles produced as described above were further treated to increase the weight increase to a total of 20%. Accordingly, to 1158.5 grams of Hybrid Urethane B were added 10.6 grams of polyaziridine crosslinker and 30.9 grams of water. The resulting mixture was stirred for 10 minutes. The fluidized bed coater was charged with 5000 grams of the particles as prepared above. The bed temperature was maintained at a value in the range of from about 93 to about 98<sup>0</sup> F. The coating material was applied at a rate of from about 70 g/min. A total of 1113.4 grams of coating material was added resulting in a weight gain of approximately 20%.

The coated particles produced as described above were further treated to increase the weight increase to a total of 28%. Accordingly, to 1158.5 grams of Hybrid Urethane B was added 10.6 grams of polyaziridine crosslinker and 30.9 grams of water. The resulting mixture was stirred for 10 minutes. The fluidized bed coater was charged with 4700 grams of the particles as prepared above. The bed temperature was maintained at a value in the range of from about 93 to about 98<sup>0</sup> F. The coating material was applied at a rate of from about 70 g/min. A total of 1160.25 grams of coating material was added resulting in a weight gain of approximately 28%.

### Example 16

## Encapsulation of Sulfamic Acid

The polyaziridine crosslinker of Example 1 (14.1 grams) and 40.2 grams of water were added to 1544.7 grams of the Hybrid Urethane C of Example B. The resulting mixture was stirred for 10 minutes. The fluidized bed coater of Example C was charged with 5000 grams of sulfamic acid. The sulfamic acid employed consisted of particles which were small enough to pass through a 10 mesh screen but did not include particles which were small enough to pass through a 50 mesh screen. The bed temperature was maintained at a value in the range of from about 93 to about 98<sup>0</sup> F. The coating mixture was applied at a rate of in the range of from about 50 to about 70 g/min. A total of 1519.5 grams of coating mixture was successfully added. After the completion of the coating operation it was observed that the sulfamic acid had experienced an apparent weight increase of approximately 12%, which increase was attributed to the Hybrid Urethane C coating material placed thereon.

The coated particles produced as described above were further treated to increase the weight increase to a total of 20%. Accordingly, to 1158.5 grams of Hybrid Urethane C were added 10.6 grams of polyaziridine crosslinker and 39.9 grams of water. The resulting mixture was stirred for 10 minutes. The fluidized bed coater was charged with 4500 grams of the

723 particles as prepared above. The bed temperature was maintained at a value in the range of  
724 from about 93 to about 98<sup>0</sup> F. The coating material was applied at a rate of from about 70  
725 g/min. A total of 1113.8 grams of coating material was added resulting in a weight gain of  
726 approximately 20%.

727 The coated particles produced as described above were further treated to increase the  
728 weight increase to a total of 28%. Accordingly, to 1158.5 grams of Hybrid Urethane C was  
729 added 10.6 grams of polyaziridine crosslinker and 30.9 grams of water. The resulting mixture  
730 was stirred for 10 minutes. The fluidized bed coater was charged with 4700 grams of the  
731 particles as prepared above. The bed temperature was maintained at a value in the range of  
732 from about 93 to about 98<sup>0</sup> F. The coating material was applied at a rate of from about 70  
733 g/min. A total of 1160.2 grams of coating material was added resulting in a weight gain of  
734 approximately 28%.

735 **EXAMPLE 17**

736 **Encapsulation of Sulfamic Acid**

737 The polyaziridine crosslinker of Example 1 (25.5 grams) and 74.7 grams of water were  
738 added to 2799.8 grams of the Hybrid Urethane D of Example B. The resulting mixture was  
739 stirred for 10 minutes. The fluidized bed coater of Example C was charged with 5000 grams of  
740 sulfamic acid. The sulfamic acid employed consisted of particles which were small enough to  
741 pass through a 10 mesh screen but did not include particles which were small enough to pass  
742 through a 50 mesh screen. The bed temperature was maintained at a value in the range of  
743 from about 92 to about 98<sup>0</sup> F. The coating mixture was applied at a rate of in the range of from  
744 about 60 to about 76 g/min. A total of 2770.0 grams of coating mixture was successfully added.  
745 After the completion of the coating operation it was observed that the sulfamic acid had  
746 experienced an apparent weight increase of approximately 20%, which increase was attributed  
747 to the Hybrid Urethane D coating material placed thereon.

The coated particles produced as described above were further treated to increase the weight increase to a total of 28%. Accordingly, to 1351.6 grams of Hybrid Urethane D were added 12.3 grams of polyaziridine crosslinker and 36.1 grams of water. The resulting mixture was stirred for 10 minutes. The fluidized bed coater was charged with 5000 grams of the particles as prepared above. The bed temperature was maintained at a value in the range of from about 93 to about 98<sup>0</sup> F. The coating material was applied at a rate of about 70 g/min. A total of 1237.5 grams of coating material was added resulting in a weight gain of approximately 28%.

### **EXAMPLE 18**

The capsules produced in Examples 14, 15, 16 and 17 were contacted with a soak solution to cause the release of the encapsulated sulfamic acid. The soak solution was prepared by adding 0.15 grams of phenolphthalein in 15 ml of isopropyl alcohol, and 0.1 ml of nonylphenol surfactant to 1000 ml of deionized water.

A quantity of encapsulated sulfamic acid produced in Example 14 was weighed into a first 125-ml Erlenmeyer flask. A quantity of encapsulated sulfamic acid produced in Example 15 (equal to the quantity from Example 14) was weighed into a second 125-ml Erlenmeyer flask. A quantity of encapsulated sulfamic acid produced in Example 16 (equal to the quantity from Example 14) was weighed into a third 125-ml Erlenmeyer flask. A quantity of encapsulated sulfamic acid produced in Example 17 (equal to the quantity from Example 14) was weighed into a fourth 125-ml Erlenmeyer flask.

The soak solution in an amount of 20 ml was then added to each of the four flasks. The contents of each flask were then titrated to the end point with 0.5 M NaOH at the times indicated in Table 7. The results of the titrations are provided in Table 7.

771

Table 7

Time hrs:min	Sulfamic Acid Released, %			
	Example 14	Example 15	Example 16	Example 17
0:10	5.18	9.27	9.93	8.84
0:20	7.55	13.10	13.5	12.70
0:40	11.10	20.82	-	20.20
1:00	14.80	26.00	-	26.60
2:00	22.00	37.00	-	39.60
3:00	27.90	43.40	-	-
4:00	32.20	48.60	-	-
5:00	36.90	52.40	-	-
7:30	43.20	59.70	-	-
overnight	63.90	77.50	-	82.7

The above data clearly illustrates the usefulness of Hybrid Urethanes A, B, C and D as

barrier coatings for sulfamic acid.

#### EXAMPLE 19

##### Encapsulation of Sodium Bromate

The polyaziridine crosslinker of Example 1 (48.0 grams) and 60.2 grams of water were

added to 4086.5 grams of the Hybrid Urethane A of Example A. The resulting mixture was

stirred for 10 minutes. The fluidized bed coater of Example C was charged with 6000 grams of

sodium bromate. The sodium bromate consisted of particles which were small enough to pass

through a 10 mesh screen but did not include particles which were small enough to pass

through a 40 mesh screen. The bed temperature was maintained at a value in the range of

from about 93 to about 98° F. The coating mixture was applied at a rate in the range from

about 40 to about 60 g/min. A total of 3465.0 grams of coating mixture was successfully added.

After the completion of the coating operation it was observed that the sodium bromate had experienced an apparent weight increase of approximately 18%, which increase was attributed to the Hybrid Urethane A coating placed thereon.

## **EXAMPLE 20**

## Encapsulation of Sodium Bromate

The polyaziridine crosslinker of Example 1 (37.2 grams) and 122.9 grams of water were added to 4042.0 grams of the Hybrid Urethane E of Example B. The resulting mixture was stirred for 10 minutes. The fluidized bed coater of Example C was charged with 7000 grams of sodium bromate. The sodium bromate employed consisted of particles which were small enough to pass through a 10 mesh screen but did not include particles which were small enough to pass through a 40 mesh screen. The bed temperature was maintained at a value in the range of from about 98 to about 103° F. The coating mixture was applied at a rate of in the range of from about 48 to about 62 g/min. A total of 3603.0 grams of coating mixture was successfully added. After the completion of the coating operation it was observed that the sodium bromate had experienced an apparent weight increase of approximately 18.3%, which increase was attributed to the Hybrid Urethane E coating material placed thereon.

The coated particles produced as described above were further treated to increase the weight increase to a total of 36%. Accordingly, to 3751.5 grams of Hybrid Urethane E were added 34.3 grams of polyaziridine crosslinker and 114.1 grams of water. The resulting mixture was stirred for 10 minutes. The fluidized bed coater was charged with 5200 grams of the particles as prepared above. The bed temperature was maintained at a value in the range of from about 98 to about 103° F. The coating material was applied at a rate of about 62 g/min. A total of 3077.8 grams of coating material was added resulting in a weight gain of approximately 36%.

## **EXAMPLE 21**

## Encapsulation of Sodium Bromate

The coating material disclosed in Norman et al (U.S. 5,373,901) was used in an attempt to encapsulate sodium bromate. Thus, 596.4 grams of water and 83.3 g of polyaziridine crosslinker were added to 2923.8 grams of the coating material disclosed in Norman et al. The fluidized bed coater of Example C was charged with 5000 grams of sodium bromate. The sodium bromate employed consisted of particles which were small enough to pass through a 10 mesh screen but did not include particles which were small enough to pass through a 50 mesh screen. The bed temperature was maintained at a value in the range of from about 100 to about 106<sup>0</sup> F. The coating mixture was applied at a rate of in the range of from about 60 to about 76 g/min. A total of 2777.6 grams of coating mixture was successfully added. After the completion of the coating operation it was observed that the sodium bromate had experienced an apparent weight increase of approximately 20% which increase was attributed to the coating material disclosed in Norman et al placed thereon.

## **EXAMPLE 22**

Capsules produced in Examples 19, 20 and 21 were contacted with 50 ml of a preheated soak solution consisting of 0.1% nonylphenol surfactant in deionized water to cause the release of the encapsulated sodium bromate. A quantity 1.5 grams of encapsulated sodium bromate was weighed and then added to the soak solution which was contained in a 2 oz jar. The test sample was allowed to stand with periodic swirling. At the times indicated in the tables below a 5.0 ml aliquot was removed and transferred to a 125 ml Erlenmeyer flask containing about 20 ml of deionized water. To the flask was added 2.0 grams of potassium iodide and 5 ml of 6N HCl. The mixture was immediately titrated to a starch-iodine end point with standardized sodium thiosulfate solution. The results of the titrations are reported in Tables 8 and 9.

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TABLE 8

Time hours	Sodium Bromate Released, %		
	Test Temperature 75° F		
	Example 19	Example 20	Example 21
0.25	1.61	0.25	2.13
1.00	13.20	0.45	7.61
2.00	27.30	-	-
3.00	-	13.20	-
4.00	53.20	-	-
6.00	-	30.90	-

TABLE 9

EXAMPLE 20				
Time hours	Sodium Bromate Released, %			
	75° F	125° F	150° F	
0.25	0.25	0.20	0.10	
1.00	0.45	0.18	0.14	
3.00	13.20	0.40	0.44	
6.00	30.91	3.46	7.07	
22.00	91.80	76.20	81.60	

863        The above data clearly illustrate the usefulness of Hybrid Urethane A and Hybrid

864        Urethane E as barrier coatings for sodium bromate and show an improved release profile as  
865        compared to capsules produced according to U.S. 5,373,901.